



Electroactive polymer-based electrochemical capacitors using poly(benzimidazo-benzophenanthroline) and its pyridine derivative poly(4-aza-benzimidazo-benzophenanthroline) as cathode materials with ionic liquid electrolyte

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HIGHLIGHTS

- A new processing technique gives polymer films with superior transport properties.
- Using this technique, Type IV capacitors were constructed.
- BBL-based capacitors store slightly more energy than a comparable Py-BBL device at low rates.
- The Py-BBL devices deliver much higher energy at higher rates.
- The Py-BBL devices were found to last least five times as long as the BBL devices.

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ABSTRACT

A novel processing technique was used to solution cast films of poly(benzimidazo benzophenanthroline), (BBL), and the novel ladder polymer poly(4-aza-benzimidazo benzophenanthroline) (Py-BBL), which were used as cathode materials in Type IV electroactive polymer-based electrochemical capacitors (EPECs). This new processing technique involves co-casting the polymer from solution with a room temperature ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIBTI). The new processing technique gave polymer films with superior transport properties and electrochemical stabilities, did not require a break-in period, and yielded higher charge capacity than the standard films. Co-cast films of BBL and Py-BBL were each incorporated into separate Type IV EPECs using poly(3,4-propylene dioxythiophene) (PProDOT) as the anode material. It was found that the PProDOT/BBL capacitors store, on average, about 50% more energy than a comparable PProDOT/Py-BBL EPEC. While PProDOT/BBL films have an energy density advantage at rates (power densities) less than 0.01 kW kg⁻¹, PProDOT/Py-BBL EPECs are capable of delivering higher energy than the BBL EPECs at rates greater than 0.01 kW kg⁻¹ (550 s per cycle). In fact, PProDOT/Py-BBL devices delivered more than ten times the energy density of PProDOT/BBL devices at 0.5 kW kg⁻¹ (50 s per cycle). The PProDOT/Py-BBL EPECs were cycled for 10,000 cycles at 65% depth of discharge and maintained 96% of the initial energy and power density, whereas the PProDOT/BBL EPECs were cycled under the same conditions and lost more than 35% of the initial energy and power density after only 2300 cycles.

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1. Introduction

Conjugated polymers have a wide range of uses due to the property changes of the materials in their different states of oxidation. From neutral light-harvesting semiconductors to doped transparent electrode materials, the uses are as wide and varied as the number of polymer systems. In the area of charge storage, as portable electronic devices become more complex, and as

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renewable energy continues to gain interest, there will be interest and strong demand for any charge storage device that can provide both higher power and energy density. Specifically, properties that are unique to capacitors (high power (high C-rates)) are increasingly gaining interest. Traditional reasons for using polymer-based systems include the potential for lighter weight, lower cost, more damage resistance and more flexible packaging.

Capacitor (NEC) and Ultracapacitor (Pinnacle) were trademarks of early electrochemical capacitor companies in the 1970s [1]. These terms have since been broadened to describe any double layer or redox capacitor with specific energy and specific power intermediate to batteries and electrostatic capacitors respectively. Typically, an ultracapacitor is a device comprised of two carbonaceous electrodes, and a supercapacitor is a similar device in which two carbonaceous electrodes are catalyzed with metal oxides such as RuO₂. The term *electrochemical capacitor* is used more generally to describe any capacitor that uses electrochemical reduction/oxidation processes to store charge. Electroactive polymer-based electrochemical capacitors (EPECs) were popularized by Rudge et al. in 1994 [1]. While there are many earlier papers that fall under the guidelines set forth by Rudge, the devices were initially described as batteries by the authors [1] and the terms ultracapacitor, supercapacitor and electrochemical capacitors are sometimes used interchangeably. Since then, a wide range of materials and architectures have been explored in electroactive polymer based capacitors.

EPECs are classified by the materials used on the anode and cathode [2–5]. Types I and II utilize p-doping polymers on both electrodes. In the charged state, one electrode is fully charged and the other electrode is completely neutral. In the discharged state, each electrode is at a partially charged state. This not only limits the capacity of the cells but also the voltage and power, since only modest average voltages are possible. In a Type III device, the same polymer is used on both electrodes, but the polymer must both n- and p-dope, and both processes must be stable. This allows a higher voltage and power since voltage of the cell is raised from 0.5 V to over 2 V in most cases [6]. We have previously introduced a Type IV EPEC category, in which different polymers are used on the anode and cathode [6], allowing for separate optimization of both the n-doping and p-doping layers. Electroactive polymer-based electrochemical capacitors (EPECs), also offer the potential for increased charge storage capacity, because the entire volume of the polymer should be available for charge storage, whereas in traditional inorganic metal oxides, only the surfaces of the particles participate in the charge storage process [7].

Poly(benzimidazo benzophenanthroline) (BBL) [8] was first introduced as a temperature resistant insulating polymer. The material is difficult to process due to its poor solubility. Jenekhe [9] later found that BBL can be dissolved at higher concentrations in nitromethane with Lewis acids such as aluminum and gallium chloride, with solution concentration as high as 20 weight percent allowed for more facile processing of thin films. The first electrochemical analyses performed on BBL were in aqueous acid [2–5]. Because the electron affinity of BBL is around 4.4 eV, reductive electrochemical doping is performed at a more positive potential than most electroactive polymers. Babel and Jenekhe [4] demonstrated BBL's utility in field effect transistors.

The ability of n-doping materials to undergo many reduction cycles is important in EPECs. In fact most Type III and Type IV EPECs are limited by the stability of the n-doping material. While BBL may be a promising material n-doping, tuning the HOMO and LUMO of BBL by adding nitrogen to the backbone—making a pyridine derivative of BBL (Py-BBL)—may further improve the electrochemical stability of the reduction process. While it is likely that incorporating nitrogen may bring the reduction potential closer to 0, this might be a worthwhile trade-off.

Ionic liquid electrolytes such as 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIBTI) have been used by our group in the past and have demonstrated to be quite effective supporting electrolytes [6]. Reasons for using ionic liquid electrolytes include their low volatility, wide temperature use window, and good electrochemical and thermal stability [10].

In this work, we present the synthesis and characterization of poly(4-aza-benzimidazo benzophenanthroline) (Py-BBL), a new pyridine derivative of the cathode material BBL. In addition, we present an analysis and comparison of thin film Type IV EPECs with a working voltages of >2.0 V using BBL and Py-BBL as cathode materials.

2. Experimental

2.1. Materials

1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIBTI) was synthesized from lithium bis(trifluoromethylsulfonyl)imide and 1-ethyl-3-methylimidazolium chloride and purified via column chromatography as reported previously [11,12]. 3,4-Propylenedioxythiophene (PProDOT) was prepared and purified according to a literature procedure [13]. 2,3,5,6-Tetraamino pyridine trihydrogen chloride monohydrate was obtained by the reduction of 2,6-diamino-3,5-dinitro pyridine with Sn⁰ and aqueous HCl [14]. 1,4,5,8-Naphthalenetetracarboxylic dianhydride (NTDA, Aldrich) was sublimed twice prior to use. Poly(benzimidazo benzophenanthroline) (BBL) and all other chemicals were purchased from Aldrich and used as received. Structures of PProDOT, EMIBTI and BBL are shown in Fig. 1.

2.1.1. Films for scanning electron microscopy

The as-received BBL was dissolved at 1 wt% in methanesulfonic acid (MSA) at 80–100 °C over 24–72 h. Additional samples of BBL in MSA were prepared containing EMIBTI (i.e. 35% BBL and 65% EMIBTI). Solutions were drop cast onto glass slides or gold coated glass slides at 140 °C in air and heated for ~2 h. The resulting brassy films were dried in a vacuum oven at 100 °C for at least 24 h under dynamic vacuum. Film samples co-cast with EMIBTI were rinsed with methanol or methylene chloride to remove residual EMIBTI. The BBL samples for scanning electron microscopy were sputter coated with iridium and electron imaging was performed using a Zeiss EVO-50 Scanning Electron Microscope (SEM). Similar processing was performed for Py-BBL films.

2.2. Synthesis of Py-BBL

Two common methods to lower the energy level of LUMO with respect to the energy level of the HOMO are to either increase

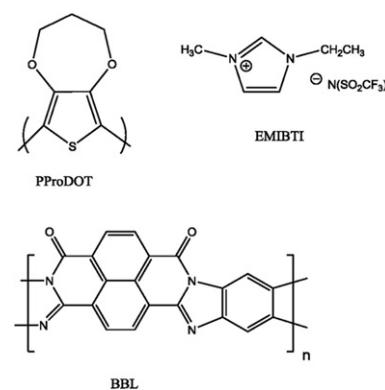


Fig. 1. Structures of PProDOT, EMIBTI and BBL.

conjugation and to introduce electron withdrawing elements. Since BBL is a conjugated ladder polymer, tuning of the orbital energy levels will require modifying the backbone structure of BBL to include electron withdrawing elements. Unfortunately, the synthesis of BBL does not allow for many options for the modification of the naphthalene monomer, but substitution of pyridine for benzene in the tetraamino monomer is possible, hence Py-BBL. This subtle change has been shown to result in an increase of electron affinity by about 0.5 eV [15]. The shifts in redox potentials can be used as a first order approximation of changes in energy levels of HOMO, LUMO or both [16].

Fig. 2 shows the synthesis of Py-BBL, which is very similar to the published procedure [17]. The free amine was generated from the tetrahydrogen chloride monohydrate by stirring the salt in polyphosphoric acid under vacuum at 80 °C. Vacuum was maintained until the mixture stopped bubbling, indicating the complete release of HCl. 1,4,5,8-Naphthalene tetracarboxylicdianhydride (NTDA) was added to the mixture, which was then heated with stirring at 120 °C under nitrogen. After the mixture became homogeneous, the reaction temperature was increased to 185 °C, and the mixture was allowed to react for 4 days with stirring. The reaction mixture was poured into water and filtered. The polymer was extracted with a Soxhlet apparatus using water then methanol and dried under vacuum at 65 °C.

2.3. Electrochemical ensemble

Electrochemistry was conducted inside of a nitrogen dry box connected to a Pine Bipotentiostat. The solvent (anhydrous propylene carbonate) and supporting electrolyte (0.1 M EMIBTI) were kept inside the dry box at all times. Sweep rate for cyclic voltammetry of BBL and Py-BBL was 100 mV s⁻¹ performed on gold barrel electrodes (Pine) with a platinum flag counter electrode and Ag wire reference electrode. The electrochemical activity of the films was performed on BBL and Py-BBL films cast onto 5 mm diameter gold button electrodes. Gold-coated barrel electrodes (0.2 cm² area) from Pine were used as current collectors.

2.3.1. Construction of Type IV devices

Poly(propylene dioxythiophene) (PProDOT) (the anode) was electrochemically polymerized onto a gold electrode using a procedure described in our earlier work [11,12]. The estimated mass of the film was between 0.5 and 0.6 mg based upon charge storage capacity (between 3 and 3.6 mC [11]). The film was stored in its neutral state by applying a voltage of -0.7 V vs Ag wire. The electropolymerized PProDOT film was carefully blotted dry with lint free paper, and then a drop of EMIBTI was placed on top of the film. Cathodes were prepared by solution casting either BBL or Py-BBL with or without ionic liquid in methanesulfonic acid using procedures similar to what we have recently reported [18]. The as-

received BBL was dissolved at 1 wt% in methanesulfonic acid (MSA) at 80–100 °C over 24–72 h. Additional samples of BBL or Py-BBL in MSA were prepared containing EMIBTI (i.e. 35% BBL or Py-BBL and 65% EMIBTI) with 1% total solutes. Solutions were drop cast (1 drop for the non-co-cast and 3 drops for the co-cast ensuring nearly identical masses) onto gold working electrodes at 140 °C in air and heated for ca. 2 h. The resulting films were dried in a vacuum oven at 100 °C for at least 24 h under dynamic vacuum. Film samples co-cast with EMIBTI were rinsed with dichloromethane and soaked in methanol to remove residual EMIBTI. The films were dried in vacuum at 60 °C. The estimated mass of the Py-BBL and BBL on the electrodes was 0.5 mg. To ensure the same mass of Py-BBL and BBL was used, we cast the films using 3 drops of the 1% total solute (EMIBTI with Py-BBL and BBL respectively) of each solution. For device construction, the cathode and anode were assembled and separated with cellulose separator paper as shown in **Fig. 3**.

3. Results and discussion

The synthesis of Py-BBL (**Fig. 2**) parallels the synthetic scheme that is used in the synthesis of BBL. The extra nitrogen lowers the energy level of the highest occupied molecular orbital (HOMO) by 0.3 eV.

In an effort to increase the initial electro-activity of BBL and Py-BBL films, EMIBTI was added to the polymer solution during the film casting process. The resultant films exhibit significantly higher electroactivity [18]. **Fig. 4** shows SEMs of BBL cast without and with EMIBTI. The films cast with the ionic liquid show significantly more porosity and voids. The increased amount of surface area that is now accessible to the electrolyte should enable faster exchange of ions in and out of the polymer layer. This increased porosity and void content per unit mass is therefore most likely responsible for the improved electroactivity. Analogous results were seen with Py-BBL films.

Films were cast both with and without ionic liquids then cycled several hundred times, and the current responses of the films were examined. **Fig. 5** summarizes the difference between the peak current density and charge capacity per gram of BBL with the ionic liquid and without the ionic liquid. The films cast with the ionic liquid show much more charge storage capability, maintain peak current and are stable over many hundreds of cycles, whereas the films cast without the ionic liquid initially show very little charge storage capability with a gradual growing in process that leveled off after 200 cycles. As shown in **Fig. 5**, after approximately 1000 cycles the coulombic capacity per gram of the film without the ionic liquid was approximately 60% of that of the capacity of the film cast with ionic liquid. Similar results were obtained with co-cast and non co-cast Py-BBL. Therefore, all device work in this study was performed with polymer films co-cast with EMIBTI.

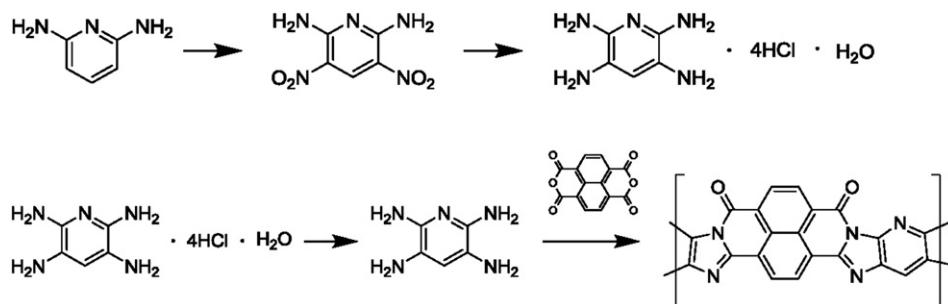


Fig. 2. Synthesis of Py-BBL.

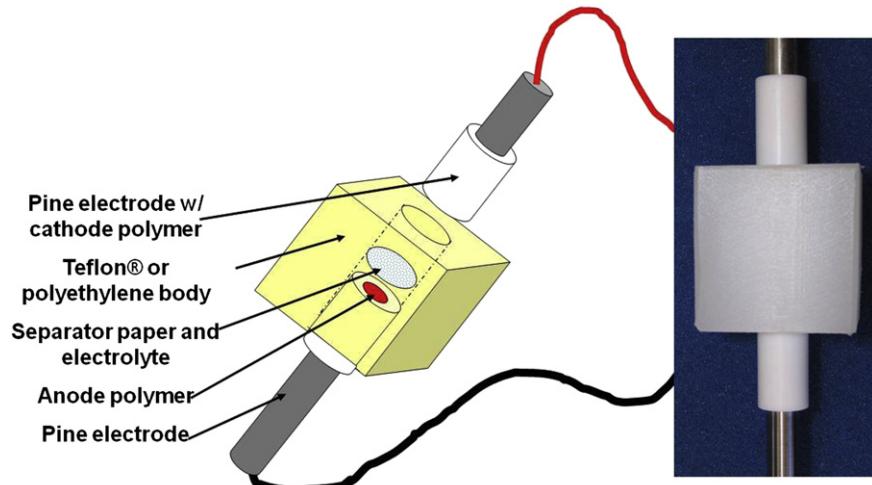


Fig. 3. Schematic construction of electroactive polymer-based electrochemical capacitors (EPECs).

3.1. Comparison of BBL and Py-BBL electrochemistry

With the utility of co-casting polymer films with EMIBTI established, our attention turned to the direct comparison of BBL

and Py-BBL electrochemical performance. Fig. 6 shows the CV properties of BBL (red) and Py-BBL (blue). The reduction potentials for BBL and Py-BBL were found to be -1.18 V and -1.00 V, respectively, at a scan rate of 100 mV s^{-1} in EMIBTI and propylene carbonate. The shift in reduction potential with Py-BBL affords a lower charging threshold with signs of capacitive behavior (a broader electrochemical response) at lower potentials (For interpretation of the references to color in this paragraph, the reader is referred to the web version of this article.).

3.2. Comparison of BBL and Py-BBL electrochemical capacitors

Type IV EPECs using PProDOT and BBL were assembled with EMIBTI as the electrolyte. The long term energy density behavior of these devices were studied at 100 mV s^{-1} and 65% depth of discharge. 65% depth of discharge was chosen to ensure that a good portion of the coulombic capacity of the devices was used (rigorous conditions) while allowing for sufficient cycles to be performed in a reasonable time frame. Cycles of charging and discharging of PProDOT/BBL capacitors from 0 V to 2.75 V over the first 300 full cycles exhibited a 25% loss of energy density. Coulombic efficiencies dropped from 93% to 75%. PProDOT/Py-BBL capacitors were cycled from 0 V to 2.00 V. After 2000 full cycles there was only 5% loss in charge capacity and coulombic efficiency of the PProDOT/Py-BBL devices generally remained greater than 95%. As seen in Fig. 7, the PProDOT/BBL device is not very stable, as evidenced by the greater than 50% loss in energy density after only 500 cycles.

The use of PProDOT and PProDOT in Type I and Type II devices has shown incredible stability with a minimal loss in activity even after one hundred thousand cycles of charging and discharging at greater than 75% depth of discharge [11]. Thus, it seems highly unlikely that PProDOT would limit the stability of the BBL-PProDOT device. Rather, the potential that is needed to charge the device most likely approaches/exceeds the window of electrochemical stability for BBL.

A PProDOT/BBL capacitor was also examined using the same testing conditions as were used with PProDOT/Py-BBL, specifically the cycling between 0 V and 2.00 V, in the hopes that a lower potential will lead to a more stable device. Cycling the PProDOT/BBL device at this lower potentials lead to a marginal increase in stability with only 20% charge capacity lost after 350 cycles, as opposed to 25%, but since the charging potential was much below that of the required threshold potential, the output voltages as well as the average current output were much lower than that of

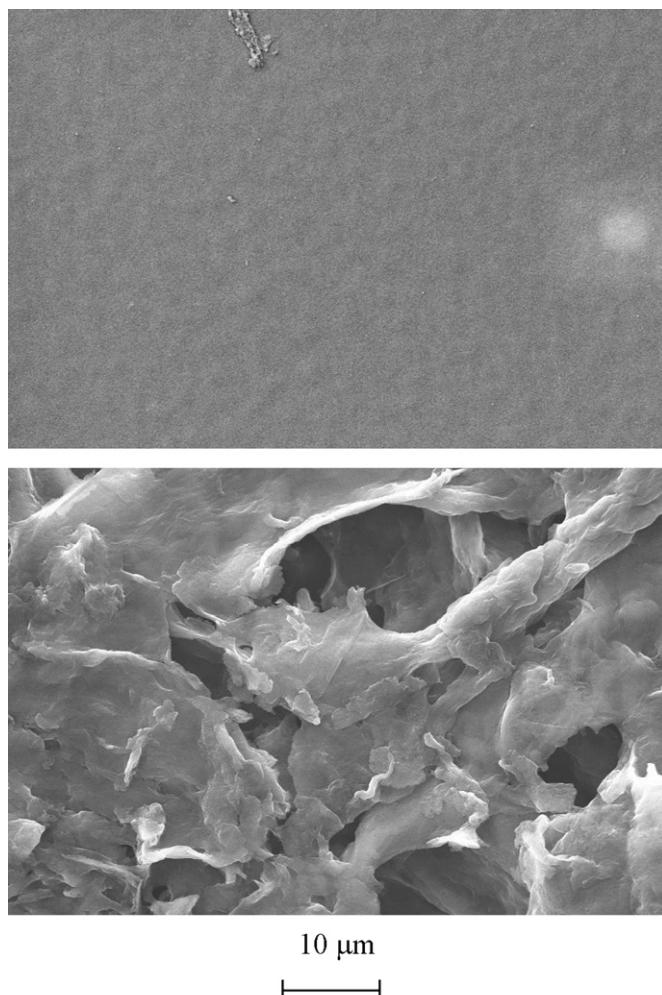


Fig. 4. Scanning electron micrographs (SEMs) of BBL films without (above) and with (below) EMIBTI in co-casting process. The scale bar is 10 μm .

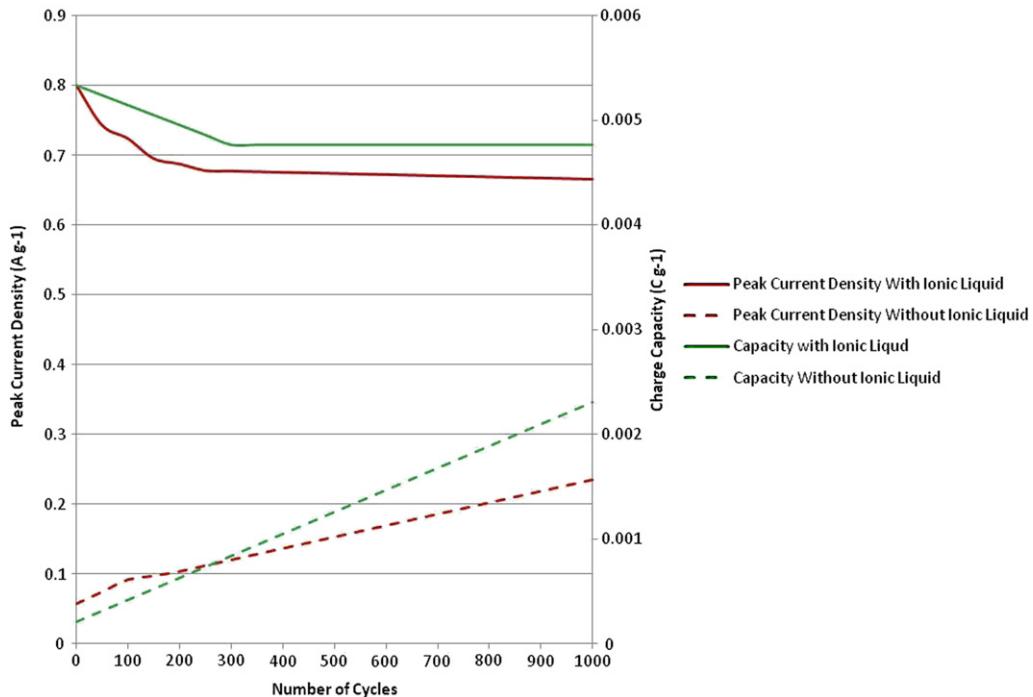


Fig. 5. Peak current density and coulombic capacity comparison between BBL with and without the ionic liquid.

a PProDOT/Py-BBL device. In other words, a PProDOT/BBL device run at 2.0 V has less capacity and lower energy density and is still less stable than the PProDOT/Py-BBL device. A PProDOT/Py-BBL decays nearly catastrophically when charged to 2.75 V.

3.2.1. Comparison of BBL and Py-BBL device energy and power densities

The PProDOT/BBL capacitor has an average output voltage of 1.375 V (maximum 2.75 V). The average voltage was taken to be

the potential at which 50% of the total charge is delivered at a lower voltage (regardless of maximum voltage), which requires a detailed analysis of the cyclic voltammetry response. The PProDOT/Py-BBL capacitor has an average output voltage of 1.00 V (maximum 2.00 V). This may lead to the conclusion that the PProDOT/BBL capacitor will deliver higher energy at all rates. However, the advantage in voltage (and hence energy density) of the PProDOT/BBL capacitor is lost at higher rates (higher power densities).

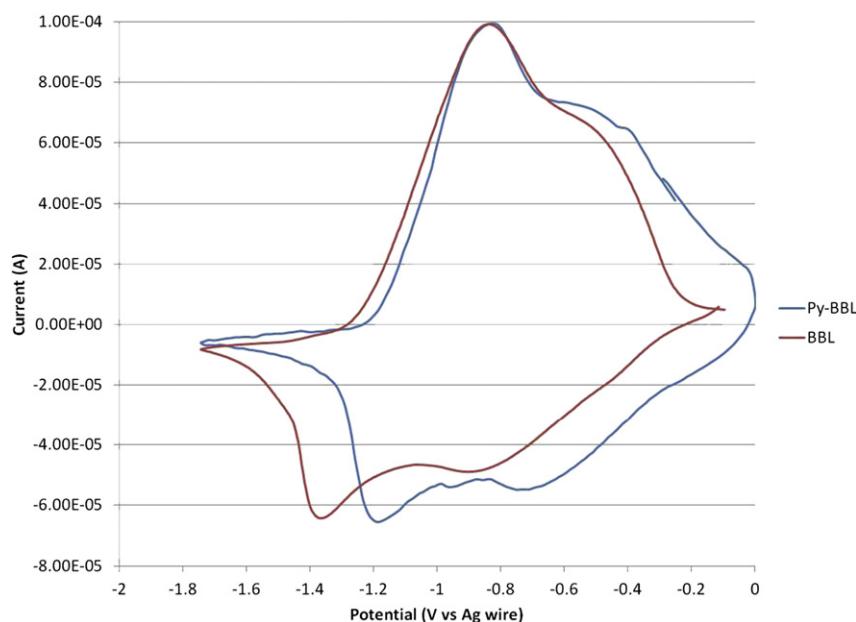


Fig. 6. Comparison of cyclic voltammetry between BBL (red) and Py-BBL (blue) 100 mV s⁻¹ versus Ag wire (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

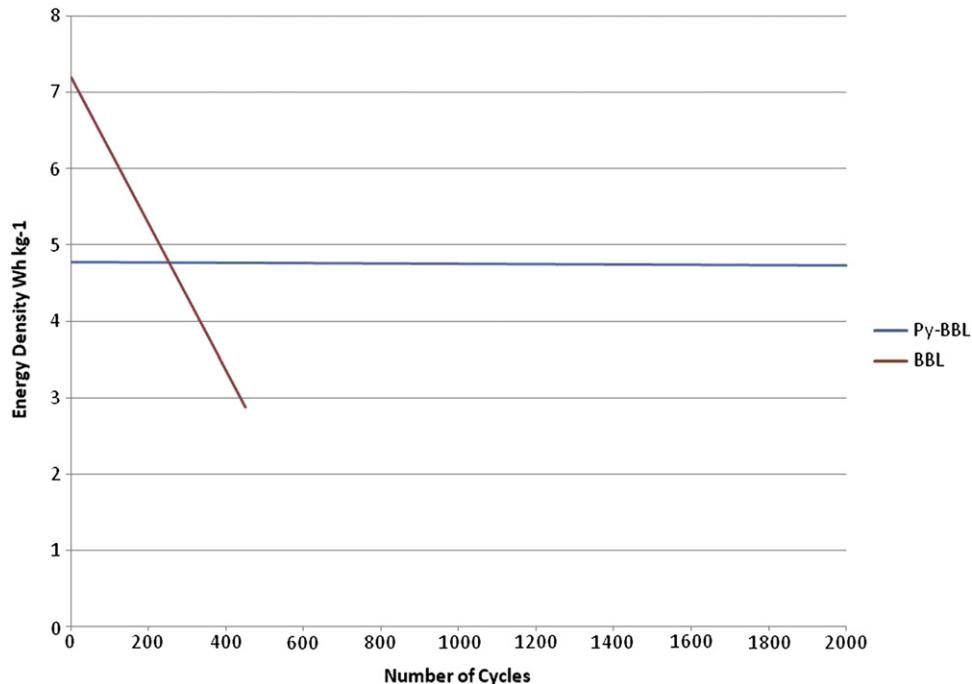


Fig. 7. Long term cycling behavior of PProDOT/Py-BBL- (blue) and PProDOT/BBL- (red) based EPECs; 2000 cycles are shown for PProDOT/Py-BBL, while 500 cycles are shown for PProDOT/BBL (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

Table 1
Summary of results for PProDOT/BBL and PProDOT/Py-BBL EPECs.

Capacitor	Rate (mV s⁻¹)	Upper potential(V)	Capacity (mC)	Average potential (V)	Energy density (Wh kg⁻¹)	Power density (kW kg⁻¹)	Loss after 350 cycles
PProDOT/BBL	10	2.75	5.8	1.375	7.2	0.013	25%
PProDOT/BBL	10	2.0	4.4	0.85	3.4	0.013	20%
PProDOT/Py-BBL	10	2.0	5.2	1.0	4.7	0.013	<1%
PProDOT/Py-BBL	10	2.75	5.3	1.15	5.1	0.013	90%

Table 1 summarizes the results for each of the EPECs studied as well as a summary of the stability of each device under the charging voltages.

While the PProDOT/BBL EPEC appears to have the energy density advantage at low rates, it is important to determine whether this energy density advantage is maintained at higher discharge rates (higher power). **Fig. 8** shows a Ragone Plot comparing the properties of Py-BBL and BBL capacitors at various power densities. Changes in power density are generally equivalent to changes in discharge rate.

As seen from **Fig. 8**, any minor advantages in energy density that the BBL capacitors have are very quickly lost at even modestly high power densities. At just slightly higher than 0.03 kW kg^{-1} power density (200 s per cycle), the energy density advantage of the BBL capacitors is completely overtaken by that of the Py-BBL supercapacitors. The energy density of the Py-BBL capacitor at approximately 0.5 kW kg^{-1} power density (50 s per cycle) is 10 times higher than that of the BBL capacitor. There is a clear advantage of the Py-BBL in both energy and power density at the higher rates. Furthermore, the Py-BBL capacitor maintains 96% of its initial energy and power densities after 10,000 cycles; the BBL capacitor loses more than 35% of its initial energy and power density after only 2300 cycles.

The superior performance of Py-BBL at higher rates could be due in part to the narrowing of the HOMO–LUMO gap, as evidenced by the shift of the reduction potential by 0.18 V. This lower energy barrier allows for a faster uptake and transfer of

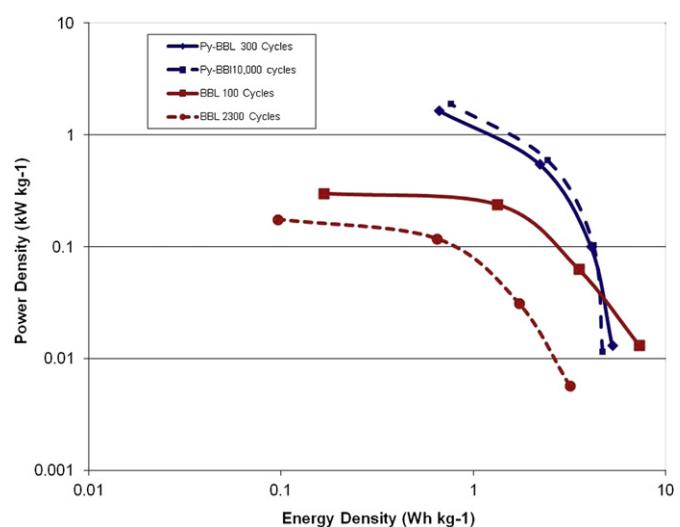


Fig. 8. Ragone plot showing performance of PProDOT/Py-BBL and PProDOT/BBL EPECs as a function of cycle number.

electrons, although it is also possible (but not obvious from the SEM photos) that the porosity of Py-BBL films is higher than the BBL films and thus allows for ions to diffuse more quickly.

4. Conclusions

A higher nitrogen analog of the ladder polymer BBL (Py-BBL) was prepared. Films of BBL and Py-BBL were co-cast from solution with a room temperature ionic liquid, EMIBTI. This process produced polymer films with superior performance at high charging rates; did not require a break-in period, and resulted in films with higher charge storage capability than the standard films. These respective films were then incorporated into Type IV electrochemical capacitors. Py-BBL-based electrochemical capacitors appear to offer superior energy and power densities over the BBL-based devices at modestly slow rates and higher. BBL films have an energy density advantage (50%) at very slow rates (550 s per cycle). Above rates of 200 s per cycle (0.01 kW kg^{-1}), PProDOT/Py-BBL electrochemical capacitors are capable of delivering significantly higher energy than the PProDOT/BBL capacitor. At 50 s per cycle (0.5 kW kg^{-1}) the PProDOT/Py-BBL capacitor offers an order of magnitude greater energy density. The PProDOT/Py-BBL devices were cycled for 10,000 cycles at 65% depth of discharge and maintained 96% of the initial energy and power density whereas the PProDOT/BBL devices were cycled under the same conditions and lost more than 35% of the initial energy and power density after only 2300 cycles.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.jpowsour.2012.07.068>.

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